METHANOL SYNTHESIS FROM CO_2 AND H_2 OVER Cu/ZnO-BASED MULTICOMPONENT CATALYSTS

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INTRODUCTION

The greenhouse effect of carbon dioxide has been recognized to be one of the most serious problems in the world, and a number of countermeasures have been proposed so far. Catalytic hydrogenation of CO_2 to produce various kinds of chemicals and fuels has received much attention as one of the most promising mitigation options. In particular, methanol synthesis by CO_2 hydrogenation has been considered to play an important role in the transportation of hydrogen energy produced from natural energy such as solar energy, hydropower and so on, as shown in Fig. 1[1]. According to some estimations[2], an electric power of 300 MWh could be obtained from a methanol fired power plant in Japan, if methanol synthesized from CO_2 and H_2 produced by a electrolysis of water using an eletcric power of 1000 MWh is transported to Japan through the system shown in Fig. 1.

A practical methanol synthesis process greatly requires a high performance catalyst, which must be highly active and selective for methanol synthesis and also stable for a long period in a continuous operation. NIRE and RITE have been doing a joint research on methanol synthesis by catalytic hydrogenation of carbon dioxide. The authors have elucidated the role of metal oxides contained in Cu/ZnO-based ternary catalysts, and then developed Cu/ZnO-based multicomponent catalysts containing two or three metal oxides [3]. Furthermore, we have examined the change in the activity of the multicomponent catalysts during a long term methanol synthesis test, and investigated the methanol synthesis over the multicomponent catalysts by using a reactor with a recycling equipment for unreacted gases.

EXPERIMENTAL

All of the Cu/ZnO-based catalysts were prepared by a coprecipitation method, which was described in detail elsewhere [4]. Two kinds of Cu/ZnO-based multicomponent catalysts named MCA ($Cu/ZnO/ZrO_2/Al_2O_3$) and MCB ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) were prepared by selecting metal oxides on the basis of the role of metal oxide. A commercial catalyst ($Cu/ZnO/Al_2O_3$) for methanol synthesis from syngas was used for comparison. A conventional fixed bed flow reactor was used both for short-term methanol synthesis tests and for long-term tests. Furtheremore, a recycle reactor equipped with a compressor for recycling unreacted gases was used for investigating practical methanol synthesis operations. The catalyst fixed in a reactor was reduced in a gas mixture of H_2 (10%) and He (90%) at 523 K with a total pressure 5 MPa. The hydrogenation of CO_2 was then carried out at 523 K with a total pressure of 5 MPa in a fixed bed flow reactor by feeding a gas mixture of H_2 and CO_2 with a mole ratio of $H_2/CO_2=3$. The reaction products were analyzed by means of gas chromatographs directly connected to the reactor. The catalyst activity was measured 2h after supplying the feed gas to the reactor except for a long term methanol synthesis test. The total copper surface area of each catalyst after the reaction (Cu_{total}) was determined by the technique of N_2O reactive frontal chromatography (RFC) after re-reducing the post-reaction catalyst with H_2 at 523 K [5].

RESULTS AND DISCUSSION

The main products of CO_2 hydrogenation over Cu/ZnO-based catalysts were methanol, CO and water. Methane, dimethyl ether and methyl formate were also detected in the reaction products, but the selectivities for the by-products were less than 0.1%.

The methanol synthesis activities which were expressed by mass-time yields of methanol (MTY), Cu_{total} and the specific activities, i.e. MTY/Cu_{total}, of Cu/ZnO-based ternary catalysts ($Cu/ZnO/M_xO_y$) containing various metal oxides were examined. Table 1 shows the activities of a Cu/ZnO catalyst and the ternary catalysts containing the optimum amounts of Ga_2O_3, Al_2O_3, ZrO_2 and Cr_2O_3, which were higher than that of a Cu/ZnO catalyst by factor of 43%, 40%, 30% and 17%, respectively.

Fig. 2 shows the methanol synthesis activity of Cu/ZnO-based ternary catalysts containing Ga_2O_3, Al_2O_3, ZrO_2 and Cr_2O_3 on varying the content from 5 to 40 wt% as a function of total Cu surface area (Cu_{total}). For each metal oxide contained in the Cu/ZnO-based catalysts, a linear relationship between MTY and Cu_{total} was seen, indicating that the specific activity is identical for each metal oxide even if the content of a metal oxide in a Cu/ZnO-based catalyst is varied. The specific activities for the Cu/ZnO-based catalysts containing Ga_2O_3 and Cr_2O_3 were greater than that of a Cu/ZnO catalyst by factor of 40% and 30%, respectively. On the other hand, the specific activity was not altered by the addition of Al_2O_3 or ZrO_2, though these metal oxides play a role in increasing Cu surface area. This indicates that the addition of Al_2O_3 or ZrO_2 improves the dispersion of Cu particles without changing the specific activity of a Cu/ZnO catalyst, while Ga_2O_3 and Cr_2O_3 are not effective for improving the dispersion of Cu, but are effective for increasing the specific activity of a Cu/ZnO catalyst.

Table 2 shows the methanol synthesis activities of the multicomponent catalysts. The activities of the multicomponent catalysts were higher than those of the ternary catalysts, and MCB exhibited the highest activity. The total Cu surface area of MCA was higher than that of $Cu/ZnO/Al_2O_3$, but the specific activity of MCA was the same as that of $Cu/ZnO/Al_2O_3$. On the other hand, the specific activity of MCB was higher than that of $Cu/ZnO/Al_2O_3$, though the total Cu surface area of MCB was a little smaller than that of $Cu/ZnO/Al_2O_3$. These findings indicate that the promoting effect of metal oxides is exerted on the multicomponent catalysts as well as on the ternary catalysts.

Fig. 3 shows the activities of the multicomponent catalysts, $Cu(50)/ZnO(45)/Al_2O_3(5)$ and $Cu(50)/ZnO(50)$ as a function of the temperature on pretreatment in H_2 ranging from 523 K to 723K. The activities of all the catalysts decreased with increasing pretreatment temperature mainly due to the decrease in Cu surface area by the sintering of Cu particles. However, the activities of MCB and MCA decreased only 10% and 15% even in pretreatment at 723 K, respectively. while the activities of the ternary catalyst and the binary catalyst decreased 30% and 85%, respectively. This suggests that the sintering of Cu particles can be suppressed by the addition of Al_2O_3, ZrO_2 and/or Ga_2O_3 to Cu/ZnO.

A methanol synthesis catalyst for a practical process is highly required to have a stable activity for a long period in a continuous operation. A long-term methanol synthesis test was performed at 523 K with a total pressure of 5 MPa by using a gas mixture of CO_2, CO and H_2, because unreacted gases and CO must be recycled to the reactor in a practical process. Fig. 4 shows the change in the activity with time on stream of MCB, which was the best catalyst among all the catalysts tested, including a commercial catalyst used for methanol synthesis from syngas. The activity of MCB decreased only by 17% in 1000 h during the test, but unchanged from 1000 h to 3400h. On the other hand, the activity of the commercial catalyst decreased by 20% in 1000 hr, and still decreased to 75% of the initial activity in 2100hr. These findings clearly indicate that the multicomponent catalyst developed in the present work is very stable for a long period in a continuous methanol synthesis operation.

Practical methanol synthesis must be performed by using a rector with recycling equipments for unreacted gases, because the conversion of CO_2 to methanol at reaction equilibrium is very low under ordinary reaction conditions, for example, 17% at 523 K and 5 MPa. Therefore, methanol synthesis using a recycle reactor was also investigated. The products of CO_2 hydrogenation at 473 K to 548 K with a total pressure of 5 MPa in the recycle reactor were methanol, CO, water, methane, ethane, dimethyl ether, methyl formate, ethanol, propanol and butanol, but the yields of the products other than methanol, CO and water were very small. The selectivity for methanol in the products except CO and water was more than 99.8%. The reaction products were cooled to 270 K in a gas-liquid separator connected to the reactor. Liquid products collected in the gas-liquid separator were taken out of the reactor, and unreacted gases as well as gaseous products such as CO, methane, ethane and dimethyl ether were recycled back to the reactor. The concentrations of methane, ethane and dimethyl ether in a recycled gas mixture remained constant after some initial period in CO_2 hydrogenation without purging unreacted gases. Table 2 shows the composition of liquid products except H_2O taken out of the recycle reactor. The purity of methanol was 99.96 wt%, and higher than that obtained in a commercial methanol synthesis from syngas. This finding suggests that the lower CO concentration in the feed gas should result in the lower yield of by-products and thus the higher methanol purity.

CONCLUSIONS

The role of metal oxides such as Ga_2O_3, Al_2O_3, ZrO_2 and Cr_2O_3 contained in Cu/ZnO-based ternary catalysts for methanol synthesis from CO_2 and H_2 was classified into two categories: to improve the Cu dispersion and to increase the specific activity.

The Cu/ZnO-based multicomponent catalysts developed on the basis of the role of metal oxides were highly active and stable for a long period in a continuous methanol synthesis operation.

The conversion of CO_2 in a make-up gas to methanol at 473 K to 523 Kwith a total pressure of 5 MPa was more than 99.9% during the methanol synthesis over the multicomponent catalyst using a reactor with a recycling equipment for unreacted gases because the yields of by-products were less than 0.1%.

In conclusion, the presented results clearly show that the Cu/ZnO-based multicomponent catalysts developed in the joint research are highly effective for a practical methanol synthesis via CO_2 hydrogenation.

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Table 1 Activities of Cu/ZnO and Cu/ZnO-based ternary catalysts containing the optimum amount of metal oxides

Catalyst	Composition (wt%)	Cu surface area[a] (m^2/g-cat)	Methanol synthesis activity[b] (g-CH_3OH/kg-cat•h)	Specific activity (mg-CH_3OH/m^2•h)
Cu/ZnO	50/50	36.5	516	14.1
Cu/ZnO/Ga_2O_3	50/25/25	37.6	738	19.6
Cu/ZnO/Al_2O_3	50/45/5	47.1	721	15.3
Cu/ZnO/ZrO_2	50/40/10	46.0	665	14.5
Cu/ZnO/Cr_2O_3	50/45/5	32.8	602	18.4

a) Total Cu surface (Cu_{total}) of the catalysts re-reduced at 523 Kafter CO_2 hydrogenation were measured by N_2O reactive frontal chromatography.
b) Reaction conditions : weight of catalyst=1 g, H_2/CO_2 ratio in the feed=3, feed gas rate =300 ml/min, temperature=523 K, total pressure=5 MPa.

Table 2 Activities of Cu/ZnO-based multicomponent catalysts

Catalyst	Cu surface area[a] (m^2/g-cat)	Methanol synthesis activity[b] (g-CH_3OH/kg-cat•h)	Specific activity (mg-CH_3OH/m^2•h)
Cu(50)/ZnO(45)/Al_2O_3(5)	47.1	721	15.3
MCA(Cu/ZnO/ZrO_2/Al_2O_3)	49.9	767	15.3
MCB(Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3)	44.5	785	17.6

a) Total Cu surface areas of the catalysts re-reduced at 523 K after CO_2 hydrogenation were measured by N_2O reactive frontal chromatography.
b) Reaction conditions : weight of catalyst=1 g, H_2/CO_2 ratio in the feed=3, feed gas rate =300 ml/min, temperature=523 K, total pressure=5 MPa.

Table 3 The composition of liquid products (except water) from a recycle reactor in this work[a], compared with that from a commercial plant for methanol synthesis from syngas[b]

Compound		Composition	
		This work	A commercial plant
Methanol	**CH_3OH**	**99.96 wt%**	**99.59 wt%**
Methyl formate	$HCOOCH_3$	330 ppm	700 ppm
Higher alcohols (C_2-C_4)	ROH	30 ppm	530 ppm
Hydrocarbons (C_6-C_{10})	C_nH_m	-	50 ppm
Dimethyl ether	$(CH_3)_2O$	-	230 ppm

a) Reaction conditions : catalyst=Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3, H_2/CO_2 ratio in the make-up gas=3, temperature=517 K, total pressure=5 MPa.
b) cited from a booklet on ICI methanol synthesis catalysts.

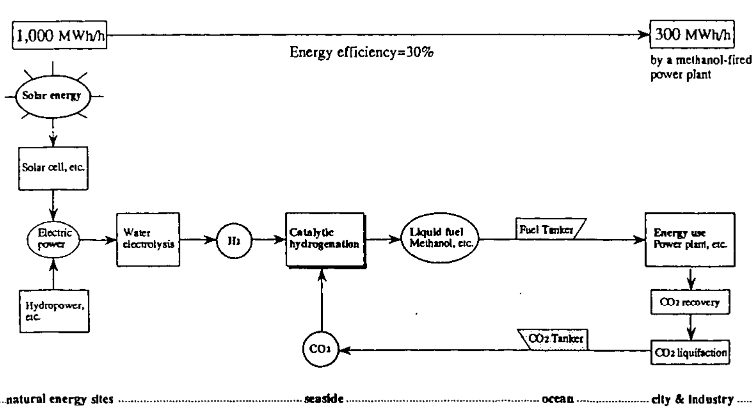

Fig. 1 Global energy network combined with catalytic hydrogenation of CO_2

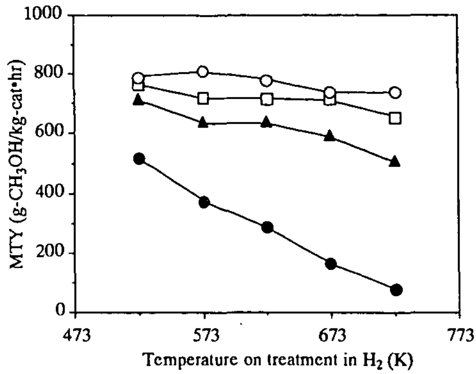

Fig. 3 Activities of various Cu/ZnO-based catalysts as a function of temperature on treatment in a stream of H_2
Reaction conditions were the same as shown in Table 1.
○:MCB($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$), □:MCA($Cu/ZnO/ZrO_2/Al_2O_3$), ▲:Cu(50)/ZnO(45)/$Al_2O_3$(5), ●:Cu(50)/ZnO(50)

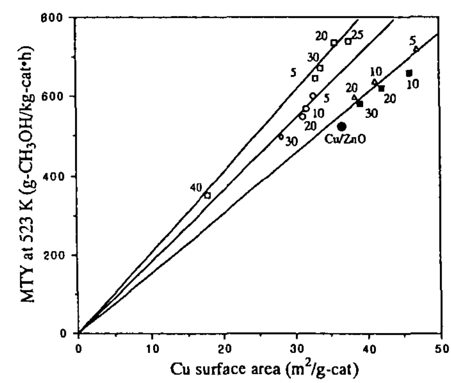

Fig.2 Methanol synthesis activity (MTY) at 523 K as a function of Cu surface area.
Reaction conditions were the same as shown in Table 1.
The contents (wt%) of metal oxides in the Cu/ZnO-based catalysts are indicated in the figure.
Cu content of the catalysts was 50 wt%.
□:$Cu/ZnO/Ga_2O_3$, ○:$Cu/ZnO/Cr_2O_3$, △:$Cu/ZnO/Al_2O_3$, ■:$Cu/ZnO/ZrO_2$, ●:Cu/ZnO (50/50).

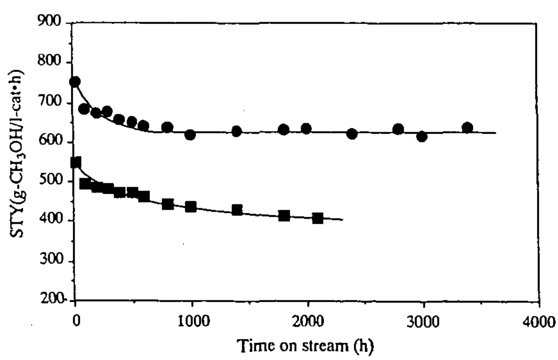

Fig. 4 Change in the activities of a multicomponent catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$, ●) and a commercial catalyst used for methanol synthesis from syngas ($Cu/ZnO/Al_2O_3$, ■) during a long-term test of methanol synthesis.
The reaction conditions: temperature=523 K, pressure=5 MPa, SV=10,000, feed gas composition=CO_2(22)/CO(3)/H_2(75).